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(21) International Application Number: PCT/US93/07455 (22) International Filing Date: 9 August 1993 (09.08.93) (30) Priority data: 07/930,971 14 August 1992 (14.08.92) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: KIM, Peter, K. ; 48 White Pine Lane, Danville, CA 94506 (US). PIERINI, Peter, E. ; 2262 Ashby Ave- nue, Berkeley, CA 940705 (US). WESSLING, Ritchie, A. ; 1126 Shattuck Avenue, Berkeley, CA 94707 (US).		(74) Agent: MAURER, Charles, J. III.; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: IMPROVED FIRE RESISTANT PANEL (57) Abstract A structural panel for a vehicle or building contains a substrate and a layer of flame-resistant polybenzazole polymer. If the substrate is heat-resistant, the panel can serve as a fire barrier. If the substrate is not heat-resistant, the polybenzazole layer can still serve to delay ignition and contain any volatile gases and molten polymer that forms when the panel is subjected to heat.		

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IMPROVED FIRE RESISTANT PANEL

This invention relates to the art of fire-resistant panels used in vehicles and
5 buildings.

Almost all natural and synthetic polymers are flammable. The flammability of
construction materials is a matter of great concern in the construction of vehicles and buildings.
This is most apparent in the construction of aircraft, ships and other mass transit vehicles, which
are regulated by the federal government, and in military transportation. However, local and
10 voluntary standards are also applied to buildings, automobiles and other places where people
may be endangered by fire. Therefore, it is very important to improve the resistance of
construction materials to fire so that fires may be prevented or the spread of fires may be
slowed to allow people to escape.

Most flame-retardants act in one of three manners: (1) a nonflammable flame-
15 retardant volatilizes in the presence of fire and inhibits the vapor phase combustion of
flammable gases produced by a flammable material; (2) the flame-retardant encourages the
substrate to undergo solid state carbonization in the presence of heat rather than producing
combustible gases; or (3) the flame-retardant forms a protective coating that insulates the
substrate from the fire. See, for example, 7 Encyclopedia of Polymer Science and Engineering,
20 Flammability, at 179-195 (J. Wiley & Sons). Thermal barriers typically work by reacting to form
an insulative coating in the presence of heat. For instance, the coating may soften and foam in
the presence of heat, then carbonize to form a rigid carbonaceous insulating foam. In places
where there is extreme danger of fire, such as military vessels and aircraft, it is also known to
put in layers of highly flame-resistant materials, such as composites of glass or carbon fibers
25 with matrices of BMI, phenolic resins, polyamide, resins, and PEEK.

Several improvements are desirable in existing fireblocking materials. For highly
fire-resistant fireblocking structures, it would be desirable to provide greater flame resistance
for improved fire protection. For more typical materials of construction it would also be
desirable to provide a fireblocking layer that can protect the material from contact with
30 ordinary small flame sources such as cigarettes, improved the resistance of the material to fire,
or protect persons near burning structures from molten and dripping polymers. What is
needed is an alternative fire-blocking material that can meet one or more of those objectives.

One aspect of the present invention is a structural panel for a vehicle or a building
that contains a supporting structure in a size and a shape that is suitable for use as a structural
35 panel for a vehicle or a building, characterized in that a continuous layer of flame-resistant
polybenzoxazole or polybenzothiazole polymer is adhered to said supporting structure.

binds

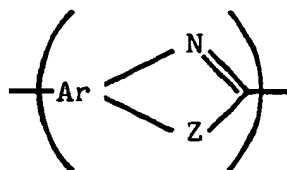
A second aspect of the present invention is a method to improve the flame-resistance of a polymer panel that is used in a vehicle or building, said method comprising the steps of:

- (1) applying to the panel a coating of dope that contains a flame-resistant polybenzoxazole or polybenzothiazole polymer and a solvent acid;
- (2) coagulating the polybenzoxazole or polybenzothiazole polymer by contact with a coagulant; and
- (3) washing the polybenzoxazole or polybenzothiazole polymer coating to remove a major portion of the solvent acid.

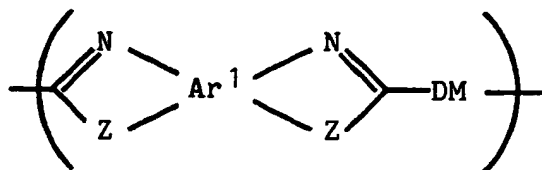
The polybenzazole polymer coatings make an excellent flame-retardant barrier. They are typically very strong, so that they do not easily break and expose the protected material to flame. They provide a high barrier to transportation of gases and liquids, so that neither molten substrates nor volatile gases given off by the degradation of the substrate can escape to harm persons or feed the flames. They are extremely flame resistant in air and are stable up to at least 600°C. Under extreme temperatures, they decompose by carbonization without the release of any appreciable amount of smoke. Depending upon the substrate, the panel may be used in buildings, aircraft, ships, submarines, automobiles, buses, trucks, trains and other forms of transportation.

The present invention uses a flame-resistant polybenzazole polymer, which is a flame-resistant polybenzoxazole (PBO) polymer or flame-resistant polybenzothiazole (PBT) polymer. The term "PBO polymer" and "PBT polymer" include random, sequential and block copolymers of those polymers. PBO and PBT polymers are described in references such as Wolfe et al., Liquid Crystalline Polymer Compositions, Process and Products, U.S. Patent 4,703,103 (October 27, 1987); Wolfe et al., Liquid Crystalline Polymer Compositions, Process and Products, U.S. Patent 4,533,692 (August 6, 1985); Wolfe et al., Liquid Crystalline Poly(2,6-Benzothiazole) Compositions, Process and Products, U.S. Patent 4,533,724 (August 6, 1985); Wolfe, Liquid Crystalline Polymer Compositions, Process and Products, U.S. Patent 4,533,693 (August 6, 1985); Evers, Thermoxadatively Stable Articulated p-Benzobisoxazole and p-Benzobisthiazole Polymers, U.S. Patent 4,359,567 (November 16, 1982); Tsai et al., Method for Making Heterocyclic Block Copolymer, U.S. Patent 4,578,432 (March 25, 1986); 11 Ency. Poly. Sci. & Eng., Polybenzothiazoles and Polybenzoxazoles, 601 (J. Wiley & Sons 1988) and W. W. Adams et al., The Materials Science and Engineering of Rigid-Rod Polymers (Materials Research Society 1989).

The polymer may contain AB-mer units, as represented in Formula 1(a), and/or AA/BB-mer units, as represented in Formula 1(b)



1(a) AB



1(b) AA/BB

wherein:

Each Ar represents an aromatic group. The aromatic group may be heterocyclic, such as a pyridinylene group, but it is preferably carbocyclic. The aromatic group may be a fused or unfused polycyclic system, but is preferably a single six-membered ring. Size is not critical, but the aromatic group preferably contains no more than 18 carbon atoms, more preferably no more than 12 carbon atoms and most preferably no more than 6 carbon atoms. Examples of suitable aromatic groups include phenylene moieties, tolylene moieties, biphenylene moieties and bis-phenylene ether moieties. Ar¹ in AA/BB-mer units is preferably a 1,2,4,5-phenylene moiety or an analog thereof. Ar in AB-mer units is preferably a 1,3,4-phenylene moiety or an analog thereof.

Each Z is independently an oxygen or a sulfur atom.

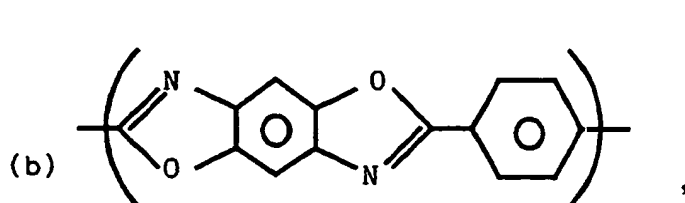
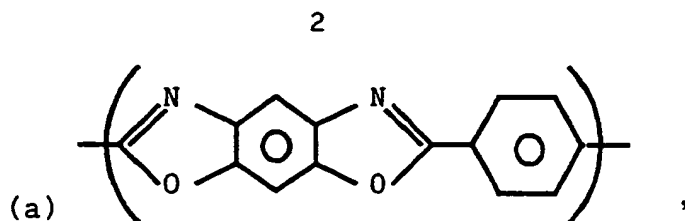
Each DM is independently a bond or a divalent organic moiety that does not interfere with the synthesis, fabrication or use of the polymer. The divalent organic moiety may contain an aliphatic group, which preferably has no more than 12 carbon atoms, but the divalent organic moiety is preferably an aromatic group (Ar) as previously described. It is most preferably a 1,4-phenylene moiety or an analog thereof.

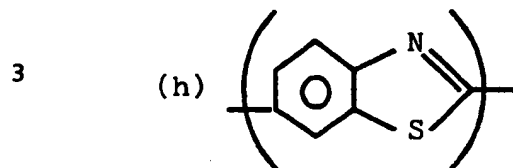
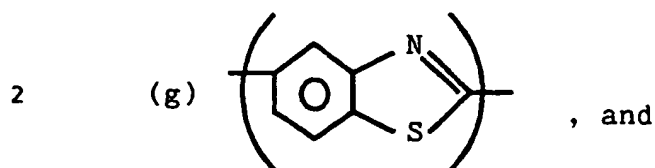
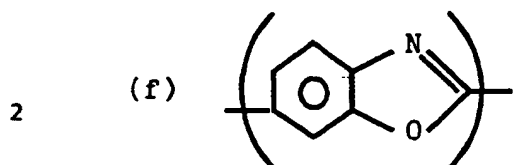
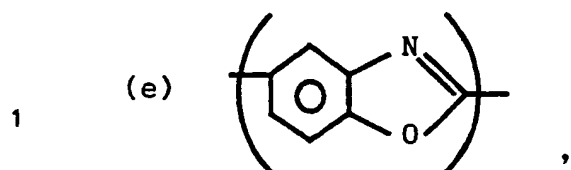
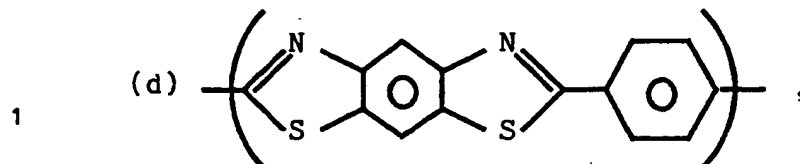
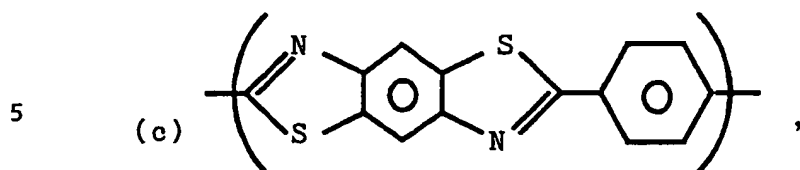
The nitrogen atom and the Z moiety in each azole ring are bonded to adjacent carbon atoms in the aromatic group, such that a five-membered azole ring fused with the aromatic group is formed.

5 The azole rings in AA/BB-mer units may be in cis- or trans-position with respect to each other, as illustrated in 11 Ency. Poly. Sci. & Eng., supra, at 602.

The polymer preferably consists essentially of either AB-PBZ mer units or AA/BB-PBZ mer units, and more preferably consists essentially of AA/BB-PBZ mer units. The polybenzazole polymer may be rigid rod, semi-rigid rod or flexible coil. It is preferably rigid rod in the case of an AA/BB-PBZ polymer or semi-rigid in the case of an AB-PBZ polymer. The
 10 polymer is preferably a lyotropic liquid-crystalline polymer (that is, it preferably forms liquid crystalline domains when it is dissolved in a solvent at a concentration greater than or equal to a critical concentration point). Azole rings within the polymer are preferably oxazole rings (Z = O).

Preferred mer units are illustrated in Formulae 2 (a)-(h). The polymer more
 15 preferably consists essentially of mer units selected from those illustrated in 2(a)-(h), and most preferably consists essentially of a number of identical units selected from those illustrated in 2(a)-(d).





35 Each polymer preferably contains on average at least 25 mer units, more preferably at least 50 mer units and most preferably at least 100 mer units. The intrinsic viscosity of rigid AA/BB-PBZ polymers in methanesulfonic acid at 25°C is preferably at least 10 dL/g, more preferably at least 15 dL/g and most preferably at least 20 dL/g. For some purposes,

an intrinsic viscosity of at least 25 dL/g or 30 dL/g may be best. Intrinsic viscosity of 60 dL/g or higher is possible, but the intrinsic viscosity is preferably no more than 40 dL/g. The intrinsic viscosity of semi-rigid AB-PBZ polymers is preferably at least 5 dL/g, more preferably at least 10 dL/g and most preferably at least 15 dL/g.

5 The polymer is typically made by solution polymerization of monomers in a dehydrating acid solvent. Examples of suitable procedures are described in Wolfe et al., U.S. Patent 4,533,693 (August 6, 1985); Sybert et al., U.S. Patent 4,772,678 (September 20, 1988); Harris, U.S. Patent 4,847,350 (July 11, 1989); Gregory, U.S. Patent 5,089,591 (February 18, 1992); and Ledbetter et al., "An Integrated Laboratory Process for Preparing Rigid Rod Fibers from the
10 Monomers," The Materials Science and Engineering of Rigid-Rod Polymers at 253-64 (Materials Res. Soc. 1989). In summary, suitable monomers (AA-monomers and BB-monomers or AB-monomers) are reacted in a solution of nonoxidizing and dehydrating acid under nonoxidizing atmosphere with vigorous mixing and high shear at a temperature that is increased in step-wise or ramped fashion from no more than 120°C to at least 190°C. Examples of suitable
15 AA-monomers include terephthalic acid and analogs thereof. Examples of suitable BB-monomers include 4,6-diaminoresorcinol, 2,5-diaminohydroquinone, 2,5-diamino-1,4-dithiobenzene and analogs thereof, typically stored as acid salts. Examples of suitable AB-monomers include 3-amino-4-hydroxybenzoic acid, 3-hydroxy-4-aminobenzoic acid, 3-amino-4-thiobenzoic acid, 3-thio-4-aminobenzoic acid and analogs thereof, typically stored
20 as acid salts.

 The process yields a dope solution that contains polymer dissolved in a solvent. The polymer may be used in the original solvent, or precipitated and redissolved in a different solvent. Some polybenzoxazole and polybenzothiazole polymers are soluble in cresol, but the solvent is preferably an acid capable of dissolving the polymer. The acid is preferably
25 nonoxidizing. Examples of suitable acids include polyphosphoric acid, methanesulfonic acid and sulfuric acid, and mixtures of those acids. The acid is preferably polyphosphoric acid or methanesulfonic acid, and is more preferably polyphosphoric acid.

 The dope should contain a high enough concentration of polymer for the polymer to coagulate to form a film or sheet of the desired thickness without substantial flaws.
30 The dope preferably contains liquid-crystalline domains. The concentration of the polymer is preferably at least 7 weight percent, more preferably at least 10 weight percent and most preferably at least 14 weight percent. The maximum concentration is limited primarily by practical factors, such as polymer solubility and dope viscosity. The concentration of polymer is seldom more than 30 weight percent, and usually no more than 20 weight percent.

35 The present invention also uses a substrate that is suitable for the intended use of the structural panel. The proper selection of substrate is dependent primarily upon the desired

use of the panel. In some cases, the purposes of the entire panel; substrate and polybenzazole layer together is to confined fire to a particularly area or protect a particular area from fire. Examples are found in aircraft, military vessels, and fire doors. The substrates in those applications should be highly flame-resistant materials that provide support for the polybenzazole layer to hold char formed by the fire in place. Suitable substrates include:

- (a) cloths of heat-resistant fibers, such as glass or carbon fibers;
- (b) heat-resistant fiber-based composites or random fiber composites that contain such heat-resistant fibers and heat-resistant matrix materials such as highly cross-length cured epoxy polymers or polycyanate polymers;
- (c) heat-resistant foams, films or sheets; and
- (d) honeycomb material containing such heat-resistant composites or films.

In applications where the panel is not meant to be a fireblocking structure but some degree of heightened flame-resistance is desired, the substrate may be almost any solid flammable structural material, although it is usually polymeric. Those polymers may optionally be foamed or in solid sheets. For example, the substrate may be polystyrene, polycarbonate, polyurethane, polymethylmethacrylate, polyethylene, polypropylene or polymethacrylamide. The substrate may even be a naturally occurring substance, such as wood.

The substrate may be in any form and size that is suitable for the intended use of the panel. It may be load-bearing or non-load-bearing. It may be suitable for interior or exterior use. It is frequently thinner in one dimension than in the other two dimensions. For example, it may be in the form of a straight or curved interior or exterior wall, in the form of a bulk head or storage container, in the form of a flooring material, or in the form of a door.

The polybenzazole layer may be applied to the substrate by any of several different methods. For instance, a film that contains polybenzazole polymer can be manufactured by extruding and stretching a dope, and then coagulating the polymer in the dope, as described in Harvey et al., Biaxially Oriented Ordered Polymer Films, U.S. Patent 4,963,428 (October 16, 1990), Fujiwara, Method for Manufacturing a Film, Japanese Kokai 63 (1988) - 74612 (April 5, 1988); Imanishi, Film Consisting of a Heterocyclic Aromatic Polymer and Its Manufacturing Method, Japanese Kokai 63 (1988) - 210138 (August 31, 1988); Lusignea, "Film Processing and Applications for Rigid-Rod Polymers", The Materials Science and Engineering of Rigid-Rod Polymers at 265-276 (Materials Research Society 1989); and Pierini et al., U.S. Serial No. 07/670,135 (filed March 15, 1991). The film may adhere to the substrate using a high temperature adhesive, such as an epoxy resin. For example, the lamination of a polybenzazole skin layer as a face sheet for a honeycomb panel is described in Lusignea et al., Film-based Composite Structures for Ultralightweight SDI Systems, PCT Publication WO 91/02646 (March 7, 1991).

Alternatively, processes for coating a substrate with a polybenzazole precursor and subsequently curing the precursor are describe in numerous references such as Angelo, et al., Polybenzoxazole Film, U.S. Patent 3,449,296 (June 10, 1969).

The polybenzazole layer is preferably applied by: (1) contacting the substrate with a dope that contains the polybenzazole polymer, (2) coagulating the polybenzazole polymer, and (3) washing away the solvent acid. The dope may be applied by ordinary methods, which will typically vary depending upon the viscosity of the dope. For instance, 5 when the substrate is a fabric, then the dope can be applied by ordinary prepregging methods suitable to the viscosity of the dope. Most polybenzazole dopes are highly viscous. They can be formed into a film as previously described and applied to a substrate by pressure at an elevated temperature. The polymer is coagulated by contact with a coagulant fluid that is a nonsolvent for the polymer and that dilutes the solvent acid. The coagulant may be organic such as 10 methanol, acetone or sulfolane. It is preferably aqueous, and most preferably water. The coagulated polymer is then washed to removed residual solvent acid.

The washing fluid has the same preferred embodiments as the coagulating liquid. The coating should be washed until sufficient acid is removed so that residues of the acid will not harm the substrate or other things that come in contact with the coating, and so that the 15 residue does not significantly reduce the mechanical properties of the polybenzazole polymer. However, the solvent acid does not always need to be entirely removed. When the solvent acid is polyphosphoric acid, low levels of phosphate residue that remain in the polymer may enhance its fire-blocking performance. The residual phosphoric acid is preferably retained as a water insoluble salt of an alkaline earth metal or a transition metal, such as magnesium, 20 calcium, zinc, titanium, aluminum, iron, nickel or cobalt. *claim 17*

The washed film is then dried by ordinary means, such as by vacuum and/or elevated temperature.

The polybenzazole polymer layer is preferably substantially continuous, so that gaps in the layer do not afford a place for fire to enter or for gaseous degradation products or 25 molten polymer to escape. It is preferably substantially impermeable to degradation products that are released by the substrate when the substrate is heated.

The polybenzazole layer may be on one or both surfaces of the substrate. Alternatively, it may be sandwiched between two layers of substrate or may be covered over by another layer to provide a desired outside surface. When the substrate comprises fibers, the 30 polybenzazole layer may serve as a matrix material to the substrate.

The polybenzazole layer should be thick enough to provide improved fire protection over the substrate alone. It is more preferably thick enough to restrain molten or gaseous material from escaping. The polybenzazole polymer layer is preferably at least 2 mil (0.05 mm) thick, more preferably at least 5 mil (0.12 mm) thick and most preferably at least 10 35 mil thick (0.25 mm). The maximum thickness is limited by practical considerations. When the polybenzazole polymer layer serves as a matrix material for a fiber substrate, it is usually impregnated throughout the fabric and may be very thick. In most cases, the polybenzazole

layer preferably makes up no more than 80 volume percent of the structure, more preferably no more than 60 volume percent and most preferably no more than 50 volume percent.

The panels may be used in an ordinary manner in vehicle and buildings. For instance they may be used as walls, floors, doors, materials for storage compartments and other surfaces in automobiles, airplanes, ships, trains, submarines and commercial and residential buildings. The panels preferably pass at least one of the following flammability tests: ASTM D1929-77, D3713-78, D2859-76, E84-84, E286-69, E162-83, E906-83 or MIL-STD 2202 (1991 version). The panels also preferably pass at least one of the following smoke tests: ASTM E662, D2843-70, or E906-83. They also preferably meet the following tests for building materials: ASTM E119-83, E136-82, D635-81, D568-77, D-3713-82, D3801-80, D2863-77, D757-77 or D1433-77.

Certain preferred aspect of the present invention are further illustrated by the following examples.

Illustrative Examples

The following examples are for illustrative purposes only. They should not be taken as limiting the scope of either the specification or the claims. Unless otherwise stated, all parts and percentages are by weight. All PBO used in the Examples is poly-(p-phenylene-cis-benzo-bis-oxazole) (cis-PBO).

Example 1- Panel Containing PBO Layer and Random Fiber Composite Substrate

A random fiber composite panel was made by the wet laid process described in U.S. Patent 4,426,470. First a random fiber composite paper was made from 40 percent chopped carbon fiber with a water dispersion sizing, 3.5 percent anionic latex, 3 percent Kevlar™ aramid pulp, 53 percent powdered 4,4'-thiodiphenyl-bisphenol A copolycarbonate and a small amount of cationic flocculant. The paper was formed and dried at 110°C for 4 to 6 hours. Three sheets of paper were layered and cured together at a temperature of 232°C for 2 minutes at 50 to 100 psi (340 to 690 kPa) and for 2.5 minutes at 500 to 1,000 psi (3500 to 6900 kPa).

A film that contained polyphosphoric acid and about 14 weight percent cis-PBO polymer having an intrinsic viscosity of 20 to 40 dL/g is placed on top of the random fiber composite panel and thermally laminated at 170°C and 200 psi (1380 kPa). The laminated panel was lofted at about 232°C and 5 psi pressure for 1 to 2 minutes using a lofting bar to achieve a thickness of 3/16 of an inch (48 mm). After cooling, the laminate was placed in a metal frame to prevent shrinkage of the PBO film and the panel was placed in water for 2 days. The panel was dried for 24 hours at 110°C.

The panel was tested using the NBS Smoke Density test (ASTM 662). The smoke density (Ds) was measured as: $132 \log(100/\% \text{-transmission})$. No smoke was measured in the smoldering mode. In the flaming mode, the smoke density after 4 minutes was 4 Ds and the smoke density at maximum was 31 Ds. The sample was also subjected to the OSU heat release

test. After 2 minutes, the heat released was 34 kW-min./m². The maximum heat released was 47 kW/m².

Example 2 - Panel Containing PBO Layer and Two Random Fiber Composite Substrate Layers

The experiment of Example 1 was repeated, except that the cis-PBO film was placed between the random fiber composite papers before they were consolidated. Under the NBS smoke release test, the smoke density was 0 Ds after 4 minutes and 32 Ds at maximum in the smoldering mode. The density was 33 Ds after 4 minutes and 55 Ds at maximum in the flaming mode.

Example 3 - Panel Containing PBO Layer Matrix Supported by Fiber Substrate

A composite that contained about 36 weight percent carbon fibers in a matrix of cis-PBO was made by the following procedure:

A dope containing 14 weight percent cis-polybenzoxazole in polyphosphoric acid was extruded from a slit die as a 15 mil thick sheet between two sheets of 2 mil thick Teflon™ fluoropolymer. Two 3 inch by 3 inch (7.5 cm by 7.5 cm) squares of the dope film were cut, and the Teflon™ sheet was stripped off of one side of each sheet. A 3 inch by 3 inch (7.5 cm by 7.5 cm) piece of Panex™ PWB-6 carbon fiber cloth, available from Stackpole Fibers Inc., was placed between the two dope film samples, with the dope sides against the carbon fiber cloth. The article was pressed at 150°C under 5 tons of pressure for one minute to form a prepreg. The prepreg was cooled to room temperature, and the Teflon™ sheet was stripped off of each side of the prepreg. The prepreg was placed in a "picture frame" holder to prevent shrinkage along the length and width of the sample but allowed shrinkage in the thickness of the sample. The framed prepreg was placed in two liters of water, left in the water for two days, removed from the frame and dried in air at ambient temperature. A composite having carbon fiber reinforcement and a cis-polybenzoxazole matrix results. The composite was cut in half. One half was placed in a heated press at 150°C and 5000 lbs (2300 kg) pressure for one minute. It was golden yellow in color.

The composite was tested using a cone calorimeter to determine ignitability, peak heat release and average heat release over 300 seconds according to ASTM E-1354. At a flux of 50 kW/m² the composite did not ignite at all. At a flux of 75 kW/m² the composite ignited after about 120 seconds. The peak heat release was about 100 kW/m² and the average heat release over 300 seconds was about 33 kW/m². At a flux of about 100 kW/m² the composite ignited after about 70 seconds. The peak heat release was about 153 kW/m² and the average heat release over about 300 seconds was about 43 kW/m².

Example 4 - PBO Sheets on Polymethylmethacrylate and High Density Polyethylene.

Sheets of cis-PBO film were attached to 1/8 inch (3 mm) thick panels of high density polyethylene (HDPE) and polymethylmethacrylate (PMMA), as shown in Table 1 below, using either a metal clamping frame or an epoxy adhesive. Laminated panels are exposed to

surface temperatures of about 825°C using a Bunsen burner on the PBO layer. The time to ignition of the PMMA or HDPE and time to burn through are shown in Table 1. A panel was also tested for smoke generation using the NBS smoke chamber test in the flaming mode (ASTM 662).

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TABLE 1

Sample	Substrate	PBO Thickness - mil (mm)	PBO Attached By	Time to Ignition (sec)	Time to Burnthrough (sec)	Smoke Density (Ds)
A	PMMA	0	-	33	93	61
B	PMMA	0	-	34	105	*
1	PMMA	2 (0.05)	Frame	600 ^a	600 ^a	90.5
2	PMMA	8 (0.2)	Epoxy	420 ^a	420 ^a	*
C	HDPE	0	-	53	170 ^b	*
D	HDPE	0	-	65	140 ^b	*
3	HDPE	10 (0.25)	Frame	600 ^c	600 ^c	*

Samples A, B, C, and D are all comparative examples, not examples of the invention.
 * - not measured

a - The PMMA slowly melted and degraded where heat was applied without ever igniting. Test was terminated after the time shown, without ignition or burn through.

b - Molten HDPA started to drip soon after ignition, and the test was terminated after the time indicated due to excessive dripping. The dripping polymer was burning.

c - The HDPA melted and degraded without ever igniting or dripping. The test was terminated after the time shown.

Example 5 - Cis-PBO Layer Laminated Directly to Foam

A dope as described in Example 1 was pressed at 150°C for 10 minutes onto a polymethacrylamide foam commercially available under the name Rohacell® 200 WF. The laminated panel was clamped in a metal frame and immersed in water for 2 days. The panel
5 was dried at 100°C for about 4 hours. The PBO surface of the panel was exposed to about 600°C using a Bunsen burner. In each case, there was no ignition of the surface exposed to flames. Foam substrate covered by 10 mL of PBO dope thermally degraded until it was completely degraded at the point of the flame after 126 and 160 seconds. Foam covered by 25 mL of PBO
10 dope thermally degraded until equivalent to a burn through after about 224 seconds.

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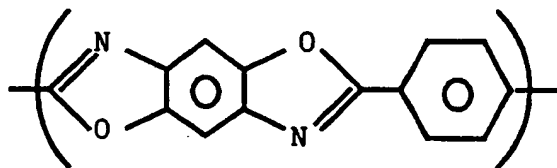
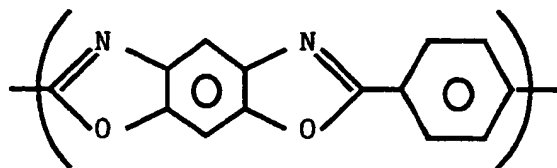
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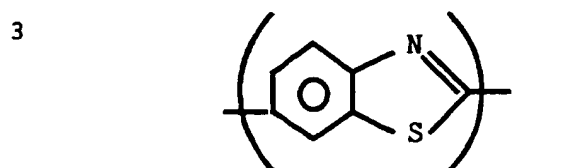
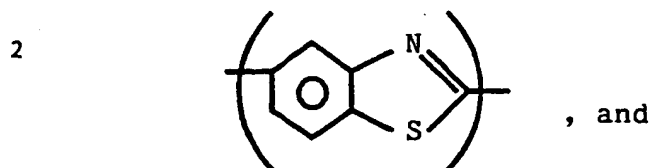
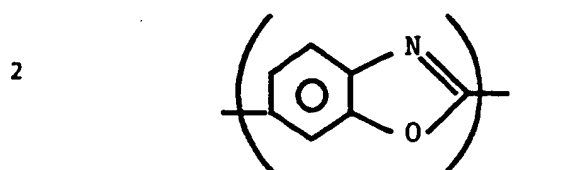
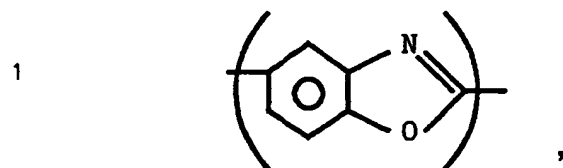
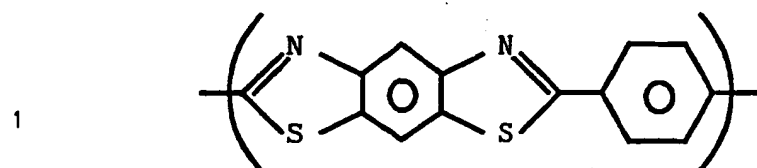
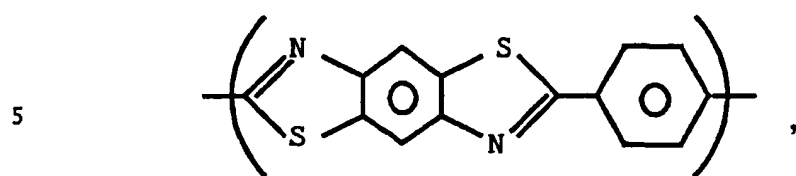
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Claims:

1. A structural panel for a vehicle or a building containing a supporting structure in a size and a shape that is suitable for use as a structural panel for a vehicle or a building, characterized in that a continuous layer of flame-resistant polybenzoxazole or polybenzothiazole polymer is adhered to said supporting structure.
2. A process to improve the flame-resistance of a polymer panel that is used in a vehicle or building, said method comprising the steps of:
 - (1) applying to the panel a coating of dope that contains a flame-resistant polybenzoxazole or polybenzothiazole polymer and a solvent acid;
 - (2) coagulating the polybenzoxazole or polybenzothiazole polymer by contact with a coagulant; and
 - (3) washing the polybenzoxazole or polybenzothiazole polymer coating to remove a major portion of the solvent acid.
3. A structural panel as claimed in Claim 1 or process as claimed in Claim 2 wherein the polybenzoxazole or polybenzothiazole polymer is a lyotropic liquid-crystalline polymer.
4. A structural panel or a process as claimed in any of the preceding Claims wherein the polybenzoxazole or polybenzothiazole polymer contains repeating units represented by any of the Formulae:





5. A structural panel as claimed in any of Claims 1, 3 or 4, wherein the substrate contains any one of:

- (a) a fiber-based composite or random fiber composite; or
- (b) a cloth of heat-resistant fibers; or
- 5 (c) a honeycomb material.

6. A structural panel as claimed in any of Claims 1, 3 or 4 wherein the substrate contains a foamed or solid sheet of flammable polymeric material.

7. A structural panel or a process as claimed in any of Claims 1, 3, 4 or 6 wherein the substrate contains wood, polystyrene, polycarbonate, polyurethane, 10 polymethylmethacrylate, polyethylene, polypropylene, or polymethacrylamide.

8. A structural panel as claimed in any of Claims 1 or 3-7 wherein the polybenzoxazole or polybenzothiazole polymer layer is adhered directly to the substrate.

9. A structural panel or a process as described in any of the preceding Claims wherein the polybenzoxazole or polybenzothiazole polymer layer is at least 0.05 mm thick.

15 10. A structural panel or a process as claimed in any of the preceding Claims, wherein the substrate is shaped for use in any one of:

- (a) an airplane;
- (b) an automobile;
- (c) a building;
- 20 (d) a train;
- (e) a bus;
- (f) a ship; or
- (g) a submarine.

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INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 93/07455

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09D179/04 C08K3/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09D C08K C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 10364 (THE DOW CHEMICAL COMPANY) 25 June 1992 see page 9, line 31 - page 10, line 14 see page 13, line 32 - line 34 see page 15, line 3-9 see claims 1,4,9	1-10
X	CHEMICAL ABSTRACTS, vol. 90, no. 22, 28 May 1979, Columbus, Ohio, US; abstract no. 170216a, SEMENOV ET AL. 'Study of polymer coatings with increased heat resistance' page 90 ; see abstract & POLIM. STROIT. MATER. 1977 , MOSCOW,USSR pages 135 - 6	1,5



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 November 1993

Date of mailing of the international search report

15. 11. 93

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GLANDDIER, A

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/US 93/07455

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING vol. 7 , 1987 , NEW-YORK, USA pages 639 - 665 HERGENROTHER 'Heat-resistant polymer' * Formula 9; Applications (pp 659-660) * see figure 2</p> <p style="text-align: center;">-----</p>	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Appl. Application No

PCT/US 93/07455

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9210364	25-06-92	US-A- 5196259	23-03-93
		EP-A- 0560897	22-09-93
		EP-A- 0560922	22-09-93
		EP-A- 0560923	22-09-93
		WO-A- 9210536	25-06-92
		WO-A- 9210527	25-06-92
